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Chemical Kinetics, an Historical Introduction

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1. Introduction

This Chapter would provide a methodological analysis of the historical developments of chemical kinetics from the beginnings to the achievements of Transition state theory and Kramers-Christiansen approach. Chemical kinetics is often treated as a side issue of the most important disciplines of chemical science. Students in most of the cases gain knowledge of Kinetics as part of Physical Chemistry introductory courses and find it again applied in many other contests.

Despite that, it would necessitate a fundamental and main teaching course as we will see in the course of this chapter. This didactical and academic approach could have many reasons. A general one may be the philosophical and psychological disposition to put our attention more on objects rather than concepts, matter over processes.

In Science History there are many examples of this tendency: the transmission of heat and electromagnetic waves are good examples. Phlogiston and Luminiferous Aether represents a materialization of processes that processes themselves do not need to be studied, however our mind need this primitive objectivization to grasp the concept in a simpler way.

This represents a fundamental issue of scientific method: to do Science we need to go beyond banality and perception. The development of Chemical Kinetics is deeply involved in the counterfactual approach that brought from Alchemy to Chemistry as for Physics form Aristotelic Natural Philosophy to Galilean Science.

2. Origins of chemical kinetics: The declinations of affinity

The chemical affinity principle, developed during the seventeenth century, derives from the alchemical concept of chemical wedding: similar substances will interact so we can categorize them. The real innovation at the end of 17th and during the 18th centuries was the application of that concept not only as a taxonomic principle but also for the comprehension of chemical reactivity.

The interaction of bodies is simpler when there is a similitude between them, this is the base idea of Chemical Affinities and come from ancient and medieval alchemy and naturalism doctrine. At the end of 17th century this intuitive principle become a theory, although qualitative, that justify and classify interactions between different substances.

In the same period also the observation of time become important for the determination of the nature of chemical reactions. Time of decurrence was clearly contemplated for the

preparation of substances with long reactions but it was seen as an ordinary technical factor. The Opera of Alchemy, for example in the transmutations of metals, was considered as a means for the acceleration of the millenary gestation of precious metals in the bowels of Earth Mother. The underestimate of real times in the alchemists conceptions resulted so natural in an activity that already theoretically reduced geological times. The paradox was that time, a fundamental principle for alchemic theory, resulted of little importance in the alchemical praxis.

Probably the first scholar that introduced a dynamical vision of the chemical phenomena was **Wilhelm Homberg (1652-1715)**. Homberg, a German scholar, worked in Magdeburg with Von Guericke, in Italy and later in England with Boyle. He introduced the first principles of quantitative measurement for chemical action: the strength of an acid towards a series of alkali depends on the time of neutralization of the various alkali.

2.1 Tabulae affinitatum

The lists of strength of alkali and the concept of chemical affinity brought **Etienne Francois Geoffroy (1672-1731)**, a French scholar initiated to chemistry by Homberg himself, to the compilation of the *Tables of Affinity*, (or Tables of Rapports) that could be considered as the first ancestor of the periodic table. The first one was done by Geffroy (Geoffroy, 1718). You can see the Encyclopédie version in the following figure.

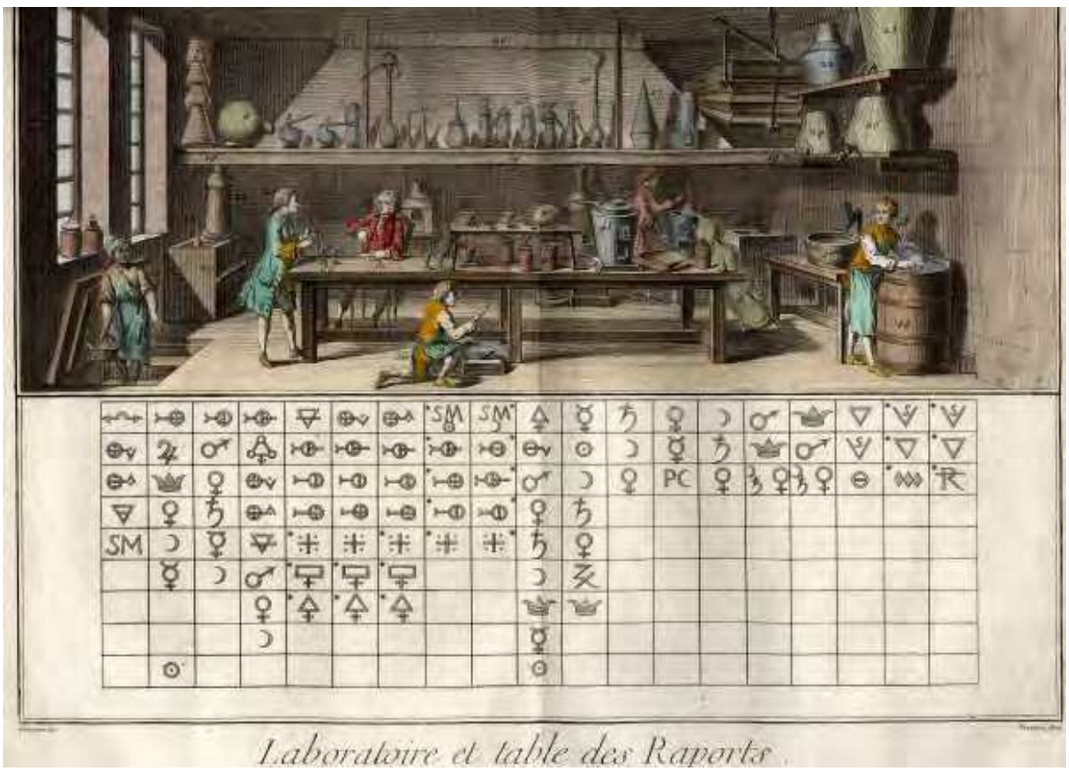


Fig. 1. Recueil de Planches, sur les Sciences, les Arts Libéraux, et les Arts Méchaniques, 1772

In the first row you can see the primary substances then going down along the columns the similar substances in order of affinity with the first one.

The development of Affinity tables was inevitably considered in the light of the main scientific discussion of the 18th century: the debate between plenistic Cartesian vision and the Newtonian distance action principle. Important chemisters of this period took parts in that debate: Boerhaave and later Buffon among Newtonian side identified affinities as a special form of gravitational attraction, Stahl on the other side negated the distance action invoking the medium of Phlogiston.

Guyton de Morveau (1737-1816), a French scholar, sustained initially phlogiston theory, but leaved it after in favor of a distance action between the different elementary particles of substances bringing the chemical affinities to a microscopic level, a similar position was taken by Berthollet and Lavoisier. De Morveau classified the kind of affinities: simple or by aggregation, composed, decomposed, double, reciprocal, intermediate, dispositional. He listed also the laws of affinity:

- Molecules have to be in fluid state to respond to affinities influence.
- Affinities acts between the elementary particles of bodies.
- Affinities between two different substances may be different from that between their composites.
- Affinity of substances acts only if it is bigger than the aggregation affinity of themselves.
- Two or more bodies united by affinity form a new body with different properties from precursors.
- Affinities action and velocity depends on temperature.

Basilar principles of Chemical Kinetics and Chemistry are going to take form. Of particular importance the last law: temperature and so ambient conditions have influence on chemical reactivity.

The position of **Torben Olof Bergman** (1735-1784), a Swedish scholar, about the influence of temperature is particularly interesting. He assumed the affinity constant at constant temperature and suggested to compile different affinity tables depending on conditions: the affinities of dry phase is different from that in liquid phase.

Bergman closed elegantly the debate on the nature of the affinities assuming a very wise position: it is not useful debating about the last nature of interacting forces between chemical particles because it will remain unknown until quantitative experiments will be done on affinities. Bergman so is the first scholar that made some hypothesis about a measure of the affinities, but their mathematical expressions and measures will be a duty for future researchers. Bergman compiled also affinity diagrams in his major opera, the **Opuscula**. They are an interesting representation of chemical reactions done with alchemical symbols: the ancestors of stoichiometric equations (although the very first one appeared even in 1615, but not systematically, in the famous **Tyrocinium Chymicum**, the first Textbook of Chemistry written by **Jean Beguin**). You can see an example in the figure 2. The diagram represents the reactions of sulfuric and hydrochloric acid with calcium carbonate and potassium hydroxide (Vitriolic and Marine for acids, Pure calcareous earth and Pure fixed vegetable alkali for the basis).

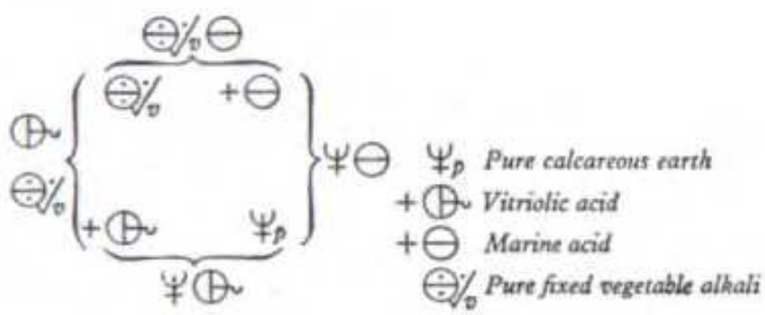


Fig. 2. This Affinity Diagram schematize two acid-base reactions

3. Chemical equilibrium conception: The law of mass action

The end of 18th Century and the first half of 19th added other essential pieces to the puzzle of Chemical Kinetics and Chemistry in general. There is a surprising absent actor in the debate on Chemical Affinities, the father of modern Chemistry: **Antoine-Laurent de Lavoisier (1743-1794)**. The Lavoisier Revolution brought quantitative measurements to Chemistry and so to Affinity Diagrams. We can see one of the first examples of stoichiometric equation from Lavoisier works in the following figure (Lavoisier 1782).

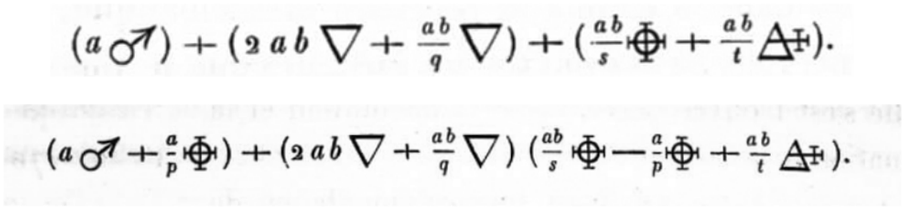


Fig. 3. Stoichimetric Equations with Lavoisier's symbols

Those symbolic equations represent one of the passages of the oxidation of iron in nitric acid where Mars symbolize iron, the nabla water, the crossed circle oxygen, the triangle and cross nitrogen oxide. In this passage iron gains the same part of oxygen that nitric acid loses, an example of the Law of Mass Conservation.

Why Lavoisier did not play a role in the debate about Affinities if he applied quantitative methods also for affinity diagrams? The causes may be many, for example the fact that he was outside main academic circles, (he was member of the French Academy of Sciences from the age of 25, but never gained an academic position). The reasons are explained by Lavoisier himself in the **Traité élémentaire de chimie**, and follow Bergan recommendations:

In this writing I followed the principle of not arguing beyond experimentations, not taking over the silence of facts. So I cannot consider those parts of Chemistry that would probably become Exact Science before the others. Scholars as Bergman, Scheele, de Morveau and many others are conducting numerous studies about Chemical Affinities and Attractions, but basic, precise and general data are lacking at the moment. Affinities theory respect to ordinary Chemistry is as Transcendent Geometry respect to Elementary one and goes over the scope of this introductory book. Mr de Morveau is writing the voice Affinity in the **Encyclopédie** *and I am worried to compete with him.*

3.1 Characterising of chemical reactions

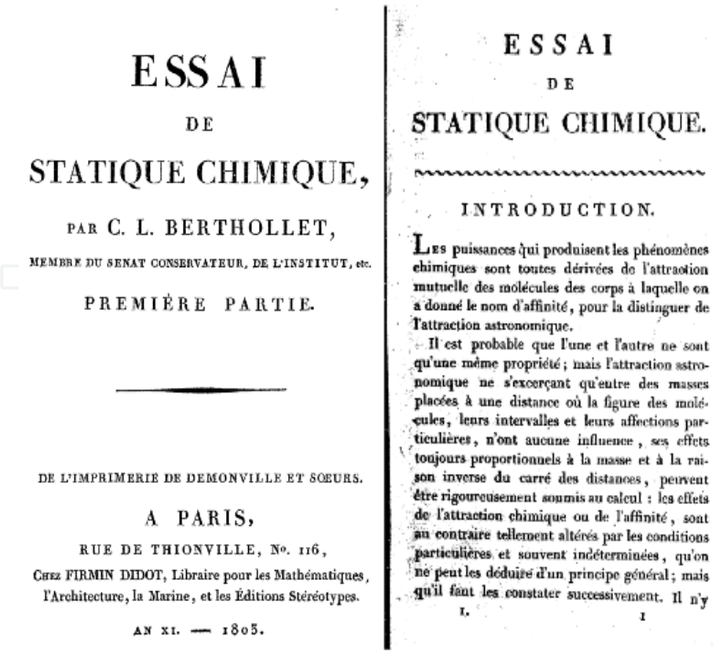
With the development of Lavoisier's methods in the second half of the 18th Century new definitions and properties are established. A concept that for today scientists results obvious was defined: the concentration of substances. The fist timid attempts to distinguish reactivity and equilibrium was made, for example sulphuric acid was considered the most powerful because it shifted other acids from their salts, the most strong because it absorbs most water, the least active because Oleum needs water or hydrated compounds to take effect. The researches about the reactions between acids and metals are of particular interest in this period. For example many scholars did not consider more metals as primary substances thinking they was compounds with an alkaline parts (it will need nearly a Century for the comprehension of redox reactions).

In the work of **Carl Friedrich Wenzel (1740-1793)**, a dresden metallurgist, we can find the first link between reaction velocity and quantity of the reactants. He investigated the reactions between metals considering the time of dissolution of little metal cylinders inside dilute acid solutions. Using Buffon theories Wenzel considered the affinity of the acids inversely proportional to the time of dissolution but considered also the role of the solvent (water). The velocity of reaction results proportional to the affinity or the strength of the acid while inversely proportional to the resistance of the solvent. In modern terms reaction velocity is proportional to concentration. Wenzel made also interesting considerations about thermal conditions, imposing the same temperature for all the dissolutions to compare them correctly. Some scholars, Wilhelm Ostwald between the most famous, awarded Wenzel for the first qualitative definition of the *Law of Mass Action*, although the primacy is commonly given to Berthollet.

Count **Claude Louis Berthollet (1748-1822)**, member of Academy of France and founder of the Ecole Polytechnique, collaborated with Lavoisier but was more lucky than him. He had no problems during the revolution and got in the good books of Napoleonic government. He followed Bonaparte's expedition to Egypt. Visiting the Natron Lakes, Berthollet observed soda deposits on the surrounding limestone hills. He supposed a chemical reaction occurring between salt (sodium chloride) and the limestone (calcium carbonate) in the hills to produce soda (sodium carbonate) and an accompanying product, calcium chloride, which seeped away into the ground. The reaction was the reverse of the one that chemists knew under laboratory conditions, and this indicated to Berthollet that physical conditions, such as heat and pressure, and quantities of reactants could affect the course of a chemical reaction.

From these and other considerations he exposed the first qualitative form of the **Law of Mass Action** during 1803 in two famous publications: "*Essai de statique chimique*" (fig. 4) e "*Recherches sur les lois des affinités chimiques*". The progress of a chemical reaction depends on the quantity and conditions of reacting substances. Berthollet's essays do not relate only on the velocity of the reaction but also on its equilibrium. Today these considerations may appear obvious but at the time they received fierce critics.

These theories and the embryonic conception of equilibrium was favourably considered by some important Chemists as Berzelius, Davy and Gay-Lussac, but most of the scientific community did not considered them being incompatible with Proust's and Dalton's Laws that monopolized the attention of the scientific community in the period.



ESSAI

DE

STATIQUE CHIMIQUE,

PAR C. L. BERTHOLLET,

MEMBRE DU SENAT CONSERVATEUR, DE L'INSTITUT, etc.

PREMIÈRE PARTIE.

DE L'IMPRIMERIE DE DEMONVILLE ET SŒURS.

A PARIS,

RUE DE THIONVILLE, No. 116,

CHEZ FIRMIN DIDOT, Libraire pour les Mathématiques, l'Architecture, la Marine, et les Éditions Stéréotypes.

AN XI. — 1803.

ESSAI

DE

STATIQUE CHIMIQUE.

INTRODUCTION.

Les puissances qui produisent les phénomènes chimiques sont toutes dérivées de l'attraction mutuelle des molécules des corps à laquelle on a donné le nom d'affinité, pour la distinguer de l'attraction astronomique.

Il est probable que l'une et l'autre ne sont qu'une même propriété; mais l'attraction astronomique ne s'exerçant qu'entre des masses placées à une distance où la figure des molécules, leurs intervalles et leurs affections particulières, n'ont aucune influence, ses effets toujours proportionnels à la masse et à la raison inverse du carré des distances, peuvent être rigoureusement soumis au calcul : les effets de l'attraction chimique ou de l'affinité, sont au contraire tellement altérés par les conditions particulières et souvent indéterminées, qu'on ne peut les déduire d'un principe général; mais qu'il faut les constater successivement. Il n'y

1. 1

Fig. 4. Title and first page of Berthollet Essay

Berthollet made other significant considerations, for example the fact that for solids the Affinity remain costant. So Affinities are not absolute but become dependant on the quantities of reactants (except solids), but how those quantities was defined? In the *Essai* he defined the Affinity $A=a/E$, where a is a constant dependant on the substance and E its equivalent weight. Multiplying the mass of the substance for unit of volume w by the precedent expression he defined the A*ctive Mass* of the reactant equal to the concentration , (numbers of equivalent per unit volume: w/E).

The reasons of this rejection depended also by the fact that most of the conclusions of Berthollet and his predecessors was qualitative and not supported by adequate analytical data. To get the first quantitative observations and thermodynamic interpretations of reacting systems we have to wait the second half of 19th Century thanks to the development of analytical chemistry.

3.2 Time: A new quantitative observable

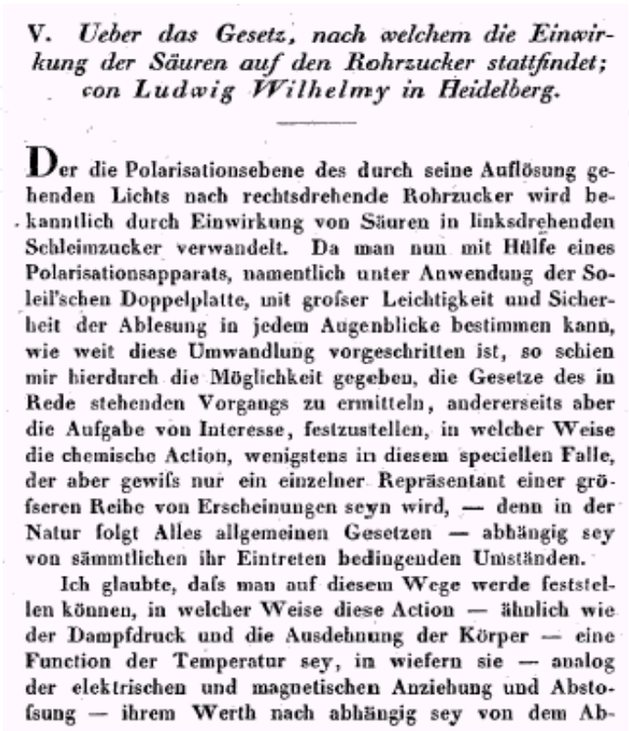
It is difficult today arguing about Chemical Kinetics without Thermodynamic but this branch of our science was established originally by simple chronological measurements of chemical processes (King 1981).

The development of quantitative relations and laws derived from the use of advanced analytical techniques but these did not give real contributions until the end of 19th Century thanks to a suitable mathematical construct.

Initially analytical observations was used to collect a multitude of data from many different systems thinking in this way to get universal laws in the optic of Natural Philosophy. It is the passage from the *many experiments* to the *good experiment* that made the true change.

The intense experimental phase around the half of 19th Century may be efficiently described by Wilhelmy and Gladstone works.

Ludwig Ferdinand Wilhelmy (1812-1864), a German physicist published in 1850 an important paper on the kinetic on the inversion of sugar with acids (Wilhelmy, 1850, Fig. 5).



V. *Ueber das Gesetz, nach welchem die Einwirkung der Säuren auf den Rohrzucker stattfindet; von Ludwig Wilhelmy in Heidelberg.*

Der die Polarisationsebene des durch seine Auflösung gehenden Lichts nach rechtsdrehende Rohrzucker wird bekanntlich durch Einwirkung von Säuren in linksdrehenden Schleimzucker verwandelt. Da man nun mit Hülfe eines Polarisationsapparats, namentlich unter Anwendung der Soleil'schen Doppelplatte, mit grofser Leichtigkeit und Sicherheit der Ablesung in jedem Augenblicke bestimmen kann, wie weit diese Umwandlung vorgeschritten ist, so schien mir hierdurch die Möglichkeit gegeben, die Gesetze des in Rede stehenden Vorgangs zu ermitteln, andererseits aber die Aufgabe von Interesse, festzustellen, in welcher Weise die chemische Action, wenigstens in diesem speciellen Falle, der aber gewifs nur ein einzelner Repräsentant einer gröfseren Reihe von Erscheinungen seyn wird, — denn in der Natur folgt Alles allgemeinen Gesetzen — abhängig sey von sämmtlichen ihr Eintreten bedingenden Umständen.

Ich glaubte, dafs man auf diesem Wege werde feststellen können, in welcher Weise diese Action — ähnlich wie der Dampfdruck und die Ausdehnung der Körper — eine Function der Temperatur sey, in wiefern sie — analog der elektrischen und magnetischen Anziehung und Abstofsung — ihrem Werth nach abhängig sey von dem Ab-

Fig. 5. Wilhelmy paper Title page

He used a new technique, Polarimetry, for evaluating the dependence of reaction velocity on the quantity of reactants and temperature. In this paper probably appeared the first differential equation used in chemistry:

$$-\frac{dZ}{dt} = MZS \tag{1}$$

Reaction velocity is the negative derivative of the sugar quantity Z in time t, S the acid quantity and M the quantity of inverted sugar in the infinitesimal time dt. Considering an excess of acid S is constant and supposing also M constant the solution results:

$$Z = Z_0 e^{-MSt} \tag{2}$$

Wilhelmy verified that M remains almost constant in time and observed the dependance of that constant with temperature.

Wilhemly's paper results impressive for its anticipations, it was written forty years before Arrhenius work on the same topic. Unfortunately, although written in a prestigious Journal, (the *Poggendorffs Annalen der Physik und Chemie*, later *Annalen der Physik*), the paper passed unnoticed by contemporary scholars. It will be rediscovered only in 1884 by Ostwald.

Not only Polarimetry but also other techniques useful for kinetic studies was developed in this period. Colorimetric titrations was used by **John Hall Gladstone** (1827-1902), Fullerian Professor of Chemistry in London, to get precise measurements of equilibrium and to investigate the effect of salts on reaction dynamic.

We will quote the conclusions of Gladstone about the action of thiocyanate on iron salts to notice the evolution of the language and concepts on the topic (Gladstone, 1855):

1. Where two or more binary compounds are mixed under such circumstances that all the resulting bodies are free to act and react, each electro-positive element arrang-es itself in combination with each electro-negative element in certain constant proportions.
2. These proportions are independent of the manner in which the different elements were originally combined.
3. These proportions are not merely the resultant of the various strengths of affinity of the several substances for one another, but are dependent also on the mass of each of tie substances in the fixture.
4. An alteration in the mass of any one of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regularly pro- gressive ratio; sudden transitions only occurring where a substance is present which is capable of combining with another in more than one proportion.
5. This equilibrium of affinities arranges itself in most cases in an inappreciably short space of time, but in certain instances the elements do not attain their final state of combination for hours, or even days.
6. The phenomena that present themselves where precipitation, volatilization, crystallization, and perhaps other actions occur, are of an opposite character, simply because one of the substances is thus removed from the field of action, and the equi-librium that was first established is thus destroyed.
7. There is consequently a fundamental error in all attempts to determine the relative strength of affinity by precipitation; in all methods of quantitative analysis founded on the colour of a solution in which colourless salts are also present; and in all conclusions as to what compounds exist in a solution drawn from such empirical rules as that " the strongest base combines with the strongest acid."

From Gladstone experiments Chemists on the field begun to use extensively optical methods verifying Berthollet's statements and two facts emerged clearly: the presence of the equilibrium conditions in contrast with Proust's Law, the hypothetical achieving of a complete reaction after an infinite time.

4. Clockwork stoichiometry

We will see that many exemplary experiments survived the second half of 19th Century and results still dominating in chemical didactics. The acid esterification of alcohols is emblematic in this sense: it is difficult nowadays to find an introductory textbook that does not explain this reaction as basic example.

In most of cases nevertheless the origin of that example is not cited. It comes from a series of experiments done by a couple of Parisian chemists around the 1860: **Pierre Eugene Marcelin Berthelot** (1827-1907) and **Leon Peon de Saint-Gilles** (1832-1863), the first one full professor of chemistry at the Ecole de Pharmacie, the second a wealthy dilettante.

Their work (Berthelot & Saint Gilles, 1862) will be extensively used by other two important couples of scholars: Guldberg and Waage, Harcourt and Esson. We will speak of them later in the chapter. In the title they referred to etherification but in the paper they speak about esterification, probably a misprint.

Arising from his interest in esterification, Berthelot studied the kinetics of reversible reactions. Working with Saint Gilles, he produced an equation for the reaction velocity depending on reactants concentrations. This was incorrect because they did not considered in the expression the inverse reaction. Other interesting considerations was the hypothesis of an exponential dependence on temperature and the fact that equilibrium position is independent from the kind of alcohols and acids used.

The conclusions of Berthelot and Sait Gilles was not particularly new compared to those of Wilhelmy. They found similar expressions and both esterification and sugar inversion are good systems for the study of kinetic and equilibrium. May be that the use of differential equations was not usual for the chemists at the time. Significantly Guldberg and Esson was mathematicians that helped later the chemists Waage and Harcourt.

The fact that chemists used mathematics so late after decades of data collections may surprise the actual reader, but we have to consider that a systematic study of mathematics was not considered in chemistry courses until after the second world war. This delay did not regarded only Chemical Kinetics but chemistry in general. We have to wait Physical Chemistry, other developments in Analytical Chemistry and a general evolution of Chemistry equipment and instruments to free chemists from very difficult and hard-working experimental praxis for the development of theoretical reflections and laws.

4.1 The law of mass action again

The first quantitative expression of the law of mass action was presented by **Cato Maximilian Guldberg** (1833-1902) and **Peter Waage** (1839-1900) two years later (Guldberg & Waage, 1864). They was Norwegian Professors of Mathematics and Chemistry at the Christiania University of Oslo and brothers in law (fig. 6).

It is interesting to consider the blessed situation of chemistry in Scandinavia coming from the necessities of mining industry and from the large number of eminent chemists like Scheele, Bergman, Berzelius, the same Guldberg and Waage, Arrhenius and Nobel later.

Scandinavian insulation and advanced knowledge promoted many autonomous researches and caused often independent contemporary discoveries with other European groups.

Despite being isolated as the use of the Laurent-Gherard notation demonstrate, (that notation was diffused more than ten years before), from 1862 and 1864 they repeated and examined experiments and results of Berthelot and Saint Gilles on esterification, Rose's work on Barium salts and that of Scherer on heterogeneous reaction between silica and soda. The study of so different processes derived from the will of the authors to get a new law, universal for all chemical processes. The style of the 1864 paper was polemical against the precedent theories of affinity that the authors considered inconclusive or erroneous.

Fig. 6. Guldberg & Waage

Guldberg and Waage preferred a less speculative and more direct approach simply enunciating the formula for the definition of action of mass and volume:

$$F_{chem} = \alpha \left(\frac{M}{V} \right)^{a} \left(\frac{N}{V} \right)^{b} \tag{3}$$

Where F_{chem} represents the chemical force, M and N the quantity of the reacting substances, V the volume, α, a and b constants wich, other conditions being equal, depends only from the nature of the substances. If one begins with a general system containing four active substances pairwise interacting, (direct and opposite reactions between two reactants and two products), and considering the balance of chemical forces Guldberg and Waage obtained the expression for chemical equilibrium:

$$\alpha \left(p - x \right)^{a} \left(q - x \right)^{b} = \alpha' \left(p' + x \right)^{a'} \left(q' + x \right)^{b'} \tag{4}$$

where p, q, p', q' are the initial concentrations of reactants and products, x the amount of transformed reactants at equilibrium reaching, α, a, b, α', a', b', constants with the previous meaning that can be calculated from the initial concentrations, the amount x and experimental data.

We can quote a passage of the 1864 paper because it resolves the apparent contradiction between affinities and equilibrium theories towards Proust's and Dalton's Laws.

That a chemical process, as so often is the case in chemistry, seems to occur in only one direction, so that either complete or no substitution takes place, arises easily from our formula. Since the active forces do not increase proportionally to the masses, but according to a power of the same, the relationship of the exponent does not have to be particularly large before the unchanged or changed amount becomes so small that it does not let itself be revealed by our usual analytical methods.

Timidly in this paper and in the following works of the two scientists there is the consciousness that the expressions derives from microscopic processes between atoms and molecules. They present a progressive clarification and distinction of the concept of chemical forces, initially considered in a Newtonian way to get the balance-equilibrium expression and in their last paper (Guldberg & Waage, 1879) assimilated to bond strength and reaction velocity, the macroscopic kinetic observable.

In this last work are present many interesting intuitions, there is an hypothesis of the microscopic interaction mechanism and from that and the stoichiometric coefficients a try to explain theoretically the exponential coefficients, previously arbitrary or purely phenomenological and there is a mild use of thermodynamic data.

Guldberg and Waage went a step further in the correct direction introducing suitable formulas for equilibrium and velocity expressions but do not have the theoretical instruments to justify and interpret it correctly. They examined a huge number of different chemical systems falling in the old trap of getting general laws from the *many experiments* rather than the *good experiment*.

5. Thermodynamics revolution

The first non systematic introduction of thermodynamics in Chemical Kinetics is due to the second couple of scientists previously cited: **Augustus George Vernon Harcourt** (1834-1919) and **William Esson** (1839-1916). Harcourt was an important chemist, member of the Royal society and president of Chemical society, Esson a mathematician and Savilian professor of Geometry. They worked at University of Oxford in a period particularly fruitful for Sciences in Britain. It is the peak of positivism and at the time different sciences, included chemistry, got clearly distinct university courses. Their activity covered a period of fifty years and represented the main passage from natural philosophy speculations to modern scientific reasoning. Influenced by Van't Hoff they will definitively abandon ambiguous terms like Affinity and Chemical Forces.

In 1864 Harcourt presented his first publications contemporary to Guldberg and Waage paper. In this work only the name of Harcourt appears but Esson asked the collaboration of a chemist around six years before to applying his mathematical methods to experimental chemistry. In 1865 it was Harcourt that asked Esson to collaborate and their partnership will continue for the rest of their lives (Harcourt & Esson 1865).

In the first part of their studies they searched chemical processes suitable for kinetics measurements. Harcourt found an initial valid system: the oxidation of oxalic acid with potassium permanganate. He supposed a two step mechanism:

1. $K_2Mn_2O_8+3MnSO_4+H_2O=K_2SO_4+2H_2SO_4+5MnO_2$
2. $MnO_2+ H_2SO_4+ H_2C_2O_4= MnSO_4+2CO_2+2H_2O$

Verifying it, like today, by the presence of the intermediate manganese oxide and by the acceleration of reaction if manganese sulphate was present at the beginning of the reaction. Examining again the data around 1866 with Esson they plotted a curve of time vs quantity of reactants verifying a logarithmic trend.

To get a better plot they needed to interrupt the reaction at will and to analyze the quantity of substances reacted at time of interruption. So they considered another reaction: the oxidation of hydroiodic acid with hydrogen peroxide in presence of definite quantities of thiosulfate and a starch indicator. They measured the time passed before the appearance of blue solutions after the consumption of thiosulfate. In this way they confirmed precisely the logarithmic trend and published their results (Harcourt & Esson, 1867).

They extended also an interesting comparison about the energetic of chemical processes. A chemical reaction is like the fall of bodies: the initial activity of reactants is converted in reaction transformation as the potential energy of a falling body in kinetic energy. Reaction velocity so does not remain constant depending on reactants activity. To get a function of velocity they need to consider an infinitesimal time interval introducing, again in analogy with Mechanics, an instantaneous reaction velocity.

The velocity of change, equal to the negative time derivative of reactants quantity, is assumed to be proportional to their original quantity y and a constant a depending on the considered system:

$$\frac{dy}{dt} = -ay \tag{5}$$

Results and methods of this system was published again and better described in other two important papers: the Bakerian Lecture (Harcourt & Esson, 1895) and the last paper written by the authors Harcourt & Esson, 1912, fig. 7).

These publications represents probably the most important works for the beginning of modern Chemical Kinetics. They introduced the today common symbol for reaction rate constant k and evaluated formally its dependence on temperature.

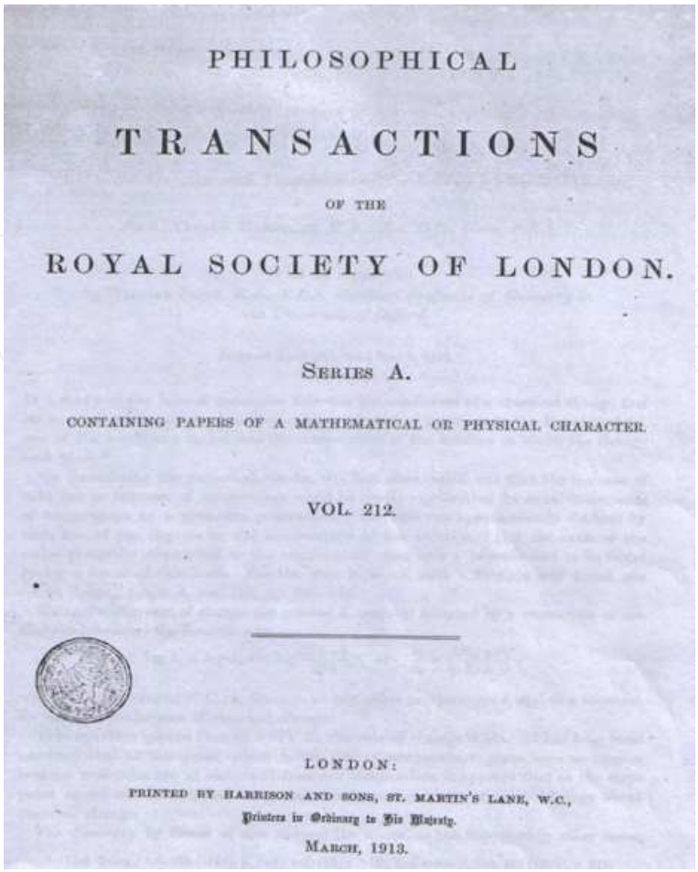
There is a clear conception of the microscopic nature of chemical processes, they supposed for example that rate constant nullifies at absolute zero, considering that inert atoms and molecules could not encounter and interact each other.

To describe temperature dependence of rate constant we will consider the theoretical explanation done by Esson from the experimental ratio between two rate constants at different temperatures found by Harcourt:

$$\frac{k}{k'} = \left(\frac{T}{T'}\right)^m \tag{6}$$

Where k, k' are the rate constants, T, T' the absolute temperatures and m an experimental pure number. Expressing the equation (6) in differential form m becomes a proportionality constant of infinitesimal changes of the temperatures and rate constants:

$$\frac{dk}{k} = m\frac{dT}{T} \tag{7}$$


PHILOSOPHICAL

TRANSACTIONS

OF THE

ROYAL SOCIETY OF LONDON.

SERIES A.

CONTAINING PAPERS OF A MATHEMATICAL OR PHYSICAL CHARACTER.

VOL. 212.

LONDON:

PRINTED BY HARRISON AND SONS, ST. MARTIN'S LANE, W.C.,

Printers in Ordinary to His Majesty.

MARCH, 1913.

Fig. 7. Front page of the Phil. Trans. volume with the last paper of Harcourt and Esson

The value of *m* resulted constant for all temperatures, depending only on the chemical system considered. Considering a big excess of one reactant its chemical activity, (Esson used the term potential but we will use activity to avoid confusion with chemical potential μ), may be supposed constant during reaction course because its quantity remain nearly the same, so the variation in rate constant may be caused only by temperature variation (the precedent argumentation for equation (5) is difficult to use in this case).

In this conditions Esson talk about stable conversion of thermal energy to chemical energy with *m* a constant of proportionality between the different energies. Reconsidering equation (5) and integrating we can obtain an expression for chemical potential energy, (in Esson's terms), whose variation remain constant for the same variation of reactant concentration at different temperatures:

$$f(y_2) - f(y_1) = f'(y_2) - f'(y_1) = kt = k't' \tag{8}$$

Where the terms with asterisk derives from a reaction at temperature *T'*. From (6), (7) and (8) equations we can obtain the following expression:

$$\frac{k}{k'} = \frac{t'}{t} = \left(\frac{T}{T'}\right)^m \tag{9}$$

Contrary to rate constant the reaction times and temperatures are measurable directly, and from the equation (9) we can obtain the value of the exponent *m*.

Once found this relationship from the careful examination of suitable reaction systems Harcourt and Esson checked its validity for a vast number of different reactions: organic, inorganic, biological, in gas phase and so on. In all cases they obtained the value of *m* different from case to case but constant for different temperatures intervals.

Many experiment of Harcourt and Esson was also considered by Van't Hoff and they correlated their law with his thermodynamic hypothesis. They found confirmation also of Van't Hoff parametric formula for *m*:

$$m = bT^{-1} + a + cT \tag{10}$$

The dependence of *m* with temperature is for example $m=a$ for dissolution of metals with acids or the action of drugs in muscles, $m=cT$ for decomposition of dibromosuccinic acid, $m=bT^{-1}$ for ethyl acetate hydrolysis with sodium hydroxide. In most of the cases *m* results constant, but Harcourt and Esson admitted that in some cases this does not happen, contradicting their hypothesis.

For the resolution of this and other problems we have to wait Van't Hoff and Arrhenius but thermodynamics got his entrance into Chemical Kinetics thanks to Harcourt and Esson extensive work, even if it is less famous than that of Guldberg and Waage.

5.1 The birth of physical chemistry

The fundamental passage for the development of modern Chemical Kinetics was done when stages of reaction was associated to definite thermodynamic states. This passage was done by a tern of important names: **Svante August Arrhenius** (1859-1927), **Jacobus Hendricus Van't Hoff** (1852-1911) and **Wilhelm Ostwald** (1853-1932), fig. 8.

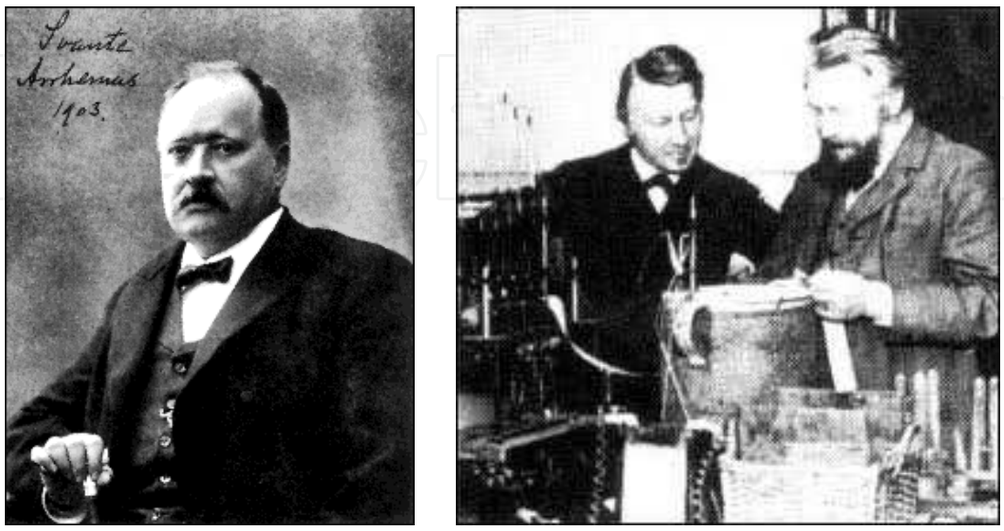


Fig. 8. From left to right: Arrhenius, Van't Hoff and Ostwald

In the first years of its construction Physical Chemistry practically corresponded to Chemical Kinetics. We will see before the contributions of Van't Hoff and Ostwald the "founders" of Physical chemistry and creators of its first journal: the "*Zeitschrift fur Physikalische Chemie*", published for the first time in 1887 at Liepzig, fig. 9.

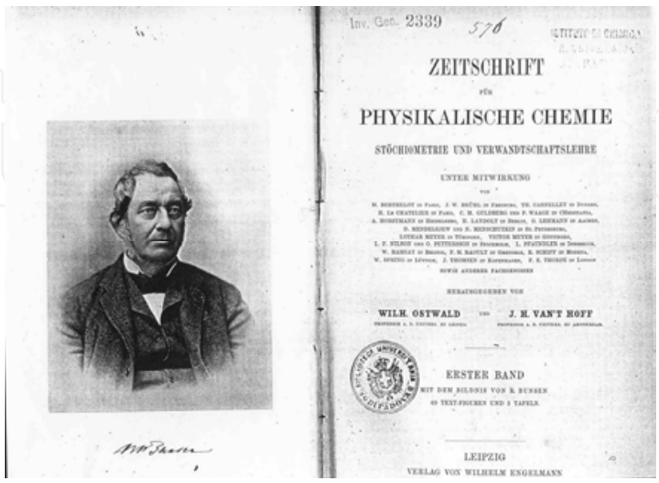


Fig. 9. Title page of the first number of the Zeitschrift

5.2 Ostwald and catalysis

Ostwald contributed directly on Chemical Kinetics less than Van't Hoff and Arrhenius, indeed he is more known for his position in the debate about atoms and for his contributions for the comprehension of Catalysis.

His main activity was done at Liepzig, where he became professor of Phisical Chemistry in 1887, after an important academic career at Riga Polytechnic where he wrote his major Opera: "*Lehrbuch der Allgemainen Chemie*", Treatise on General Chemistry, a reference book for chemistry for many years later. In 1909 he won the Nobel Price for Chemistry thanks to his work on Catalysis. In this period he partially accepted the existence of atoms after the results of Perrin and Einstein on Brownian motion.

Even if his direct contribution on Chemical Kinetics was limited it was a field that interested him for all his academic career. His first publications regarded the verification of the Law of Mass Action on different salts hydrolysis reactions (Ostwald, 1879-1884). He later rediscovered also the work of Wilhelmy on the inversion of sugar supposing erroneously that the acids do not react directly but act as accelerator (Ostwald, 1884). That erroneous interpretation was the origin of his interest on catalytic phenomena that we will treat briefly being only partially related at the scope of the chapter.

Catalysis was discovered in the first half of 19th Century and initially was considered only as a physical action. After Berzelius studies in this field the phenomenon was considered as a chemical one and its action extended for all chemical reactions.

Liebig, a pupil of Berzelius, viewed the phenomenon in terms of the radical theory: Catalysis manifests when the forces of attraction between radicals, (activated species in modern terms), are changed due to the contact with a third body that does not combine with the original reacting species.

The explanations of Catalysis was also considered from an energetic point of view: Mitschelich, Mayer and others thought it as a sort of trigger that discharged an hidden chemical energy by physical contact.

Ostwald merged the two approaches: there is not a direct physical catalytic force or action nor a direct modification of the chemical bonds but the thermodynamic of the whole system is changed with new ways of lower free energy in the chemical transformation (Ostwald, 1902). Substantially the actual conception of the phenomena.

He pointed out that the development of the new theory of Catalysis was not possible without the development of Chemical Kinetics because it was deeply involved with the velocity of reaction (Ostwald, 1909). The correct interpretation of Catalysis was one of the first big success and confirmation of the Kinetic Theory. We are in debt with Ostwald also for the popularization of Gibbs work, not very known until the end of the 19th Century.

5.3 The link between K and *k*: Van't Hoff

Jacobus Hendricus Van't Hoff (1852-1911), was a Dutch Chemist that worked in Holland and France before joining Ostwald in Germany. He gave essential contribution to many fields of chemistry and physics: from the conception of Stereochemistry (Van't Hoff, 1875), to the thermodynamic explanations of Osmosis and solutions dynamics (Van't Hoff. 1885). For his studies on solutions he won the Nobel Prize for Chemistry in 1901.

His essential contributions to Chemical Kinetics, besides the part previously cited in the first part of this chapter, culminated in the discovery of the relation between the rate constant and the equilibrium constant (Van't Hoff, 1884). He interpreted the Chemical Equilibrium as the balance between opposite reactions so he related equilibrium constant to the ratio of the rate constants of the direct and reverse reaction. From an application of Clausius-Clapeyron equation Van't Hoff found the dependence of the equilibrium constant K from the absolute temperature T:

$$\ln K = -\frac{Q}{RT} + C \tag{11}$$

Where Q represents the isochoric heat of reaction, C an arbitrary integration constant and R the gas constant.

Equilibrium constant dependence on temperature is different for exothermic and endothermic reactions, Van't Hoff called this conclusion mobile equilibrium, a principle that Le Chatelier generalized in the same period. From the equation (11) and the relation of K with the rate constants he obtained the phenomenological equation for the dependence of the rate constant k with temperature:

$$\frac{d\ln k}{dT} = \frac{A}{T^2} + B \tag{12}$$

Where A is related to some not specified heat and B remain indeterminate. In his later works he determined experimentally the values of these constants for many reactions but did not obtain a theoretical interpretation of them.

Van't Hoff classified chemical reactions at microscopic level as mono-bi and poly molecular processes, interpreting the polymolecular processes from their stoichiometry as a sequence of mono and/or bimolecular steps. From these conclusions and the equation (12) Arrhenius will get the basis for his studies.

5.4 The Arrhenius equation

The first hypothesis on the conductibility of ions in electrolytic solutions and on the electrolyte dissociation of acid and basis of the young Swedish chemist **Svante August Arrhenius** (1859-1927) was not well accepted in his own country. He searched abroad a support for his studies and obtained it from Ostwald and Van't Hoff. He worked with them for six years between 1885 and 1891 and wrote an important paper in 1887 (Arrhenius, 1887). From thereafter his theories on ionic mobility received attention and acceptance and he won the Nobel Prize for chemistry in 1903. After the german period he returned to Sweden and studied the application of Physical chemistry to biology processes giving the basis for Biochemistry (Arrhenius, 1915).

With Ostwald and Van't Hoff he worked also on the Kinetics of electrolyte solutions and exposed his most important conclusions in a fundamental paper (Arrhenius, 1989) where he reconsidered the classical case of inversion of sugar with acids.

Arrhenius wanted to obtain the phenomenological coefficients of the precedent formulas from the number of ions in solution but found discrepancies between excepted and experimental data at high temperatures. Considering also the contributions due to more frequent collisions with the help of kinetic theory of gases applied to liquid phase he estimated a variation of 2% but the discrepancies was higher, around 15%. Moreover the acidity of the solution, or the number of H^+ ions, vary very slowly with temperature (around 0.05% for K°).

What really react therefore to justify a so big dependence with temperature? Arrhenius assumed the existence of a new specimen in the reaction: the active sugar. It is the number of molecules of active sugar that determine the velocity of reaction, they are the true reacting species. There is another subordinate equilibrium inside the reaction between sugar and active sugar that determinate its kinetic.

He reinterpreted the rate constant as the ratio between the quantities of active and total sugar and evaluated its dependence in function of the temperature:

$$\frac{d\ln k}{dT} = \frac{q}{2T^2} \tag{13}$$

It is no more necessary to define the constant B from (12) and A is now $q/2$ the half heat of activation of sugar. Arrhenius valuated also successfully the question of the activated part of the acid adding different electrolytes to solution.

The equation for the dependence of velocity of reaction with temperature results:

$$\nu_1 = \nu_0 e^{\frac{q(T_1 - T_0)}{2T_1T_0}} = v_0 e^{-q\left(\frac{1}{T_1} - \frac{1}{T_0}\right)} \tag{14}$$

Where v_1 and v_0 are the velocities at temperatures T_1 and T_0. From equations (13) and (14) he obtained directly his famous formula for the rate constant:

$$k = Ae^{-\frac{E}{RT}} \tag{15}$$

Where A is a frequency factor and E the energy of activation. The essential is the introduction of the concept of activation, but the physical explanation of the constants remained vague.

6. Genesis and development of transition state theory

Van't Hoff, Arrhenius and Ostwald put the foundation for a formal systematization of Chemical Kinetics but did not achieve a self-consistent theory. Thermodynamics alone was able to treat the reactions from a macroscopic point of view, but results insufficient to fully interpret the microscopic processes.

To get a exhaustive picture of the mechanisms from at atomic or molecular scale we will need the application of Statistical Mechanics and the development of Quantum Physics.

This is the mainly reason why we have to wait around forty years before a new for a new breakthrough in Chemical Kinetics.

Anyway this forty years are characterized by many debates and other discoveries in this field (Laidler & King 1983). First of all the Arrhenius equation, mainly welcomed, created some perplexities in the researchers that studied particular class of reactions where its use was really problematic.

Max Bodenstein (1871-1942), a German physical chemist from Heidelberg that collaborated with Walter Nernst in Gottingen and took his chair at the Berlin University after his retirement, was one of these researchers.

Bodenstein worked on gas reactions dynamics at the end of 19th Century (Bodenstein, 1899). Reactions in gas phase presents more difficulties and peculiar behaviors respect to liquid ones. Bodenstein accepted the hypothesis of activated species but supposed apparent or false equilibria between them and stable reactants especially for the particular systems he examined. Bodenstein intuited a fully new class of phenomena, what we now call non-equilibrium processes, and initially provoked some interest, but this concept was too early to get a development at the time. Theoretical basis for Transition State Theory, (hereafter called TST), needed a true equilibrium state and this approach become dominant. Other important contributions due to Bodenstein was in clarifying mechanisms of many heterogeneous and catalyzed reactions and the discovery of the mechanism of Chain Reactions around 1920, a field that we will reconsider later analyzing Christiansen work.

In this period there was a great attention about the molecularity of mechanisms and of particularly interest was a debate about unimolecular reactions. The debate was that about the so called Radiative Theory (King & Laidler, 1984), proposed mainly by **Jean Baptiste Perrin** (1870-1942), around 1917. Perrin proposed that unimolecular processes was activated only by blackbody radiation. The hypothesis, fallacious, continued for nearly ten years involving many and important figures as Einstein for example. Even being wrong Radiative Theory represents an interesting case study and boosted the research on different activation causes other than thermal collisions.

Between 1920 and 1930 many scholars like Wigner, Pelzer, Polanyi and Eyring at the Haber Laboratory of the Kaiser Wilhelm Institut of Berlin established a rigorous statistical approach to Chemical Kinetics (Polanyi & Wigner, 1928; Wigner & Pelzer, 1932). Important contributions in this sense was done also by Marcelin, that introduced the modern terminology and the Gibbs standard energy of activation, and Kramers & Christiansen (Kramers & Christiansen, 1923).

6.1 Quantum mechanical interpretation

After the achievement of the wave equation for the hydrogen molecule due to Heitler and London the Hungarian **Michael Polanyi** (1891-1976), director of the Haber Laboratory in Berlin, and his host, the young Mexican American, **Henry Eyring** (1901-1981) wanted to apply it to the quantum mechanical description of the reaction of atom exchange between ortho and para hydrogen molecules: $H + H_2(orto) = H_2(para) + H$.

They generalized that description for others bimolecular gas reactions between trhee atoms in a fundamental paper in 1931 (Eyiring & Polanyi 1931). The energy of the molecular and atom states during reactions was eventually exactly calculated thanks to Quantum Mechanics. They obtained the bond and activation energies plotting the energy in function of the distance between the atoms and molecules involved in the process and built the first diagrams of potential surfaces vs reaction coordinates. You can see an example in fig. 10.

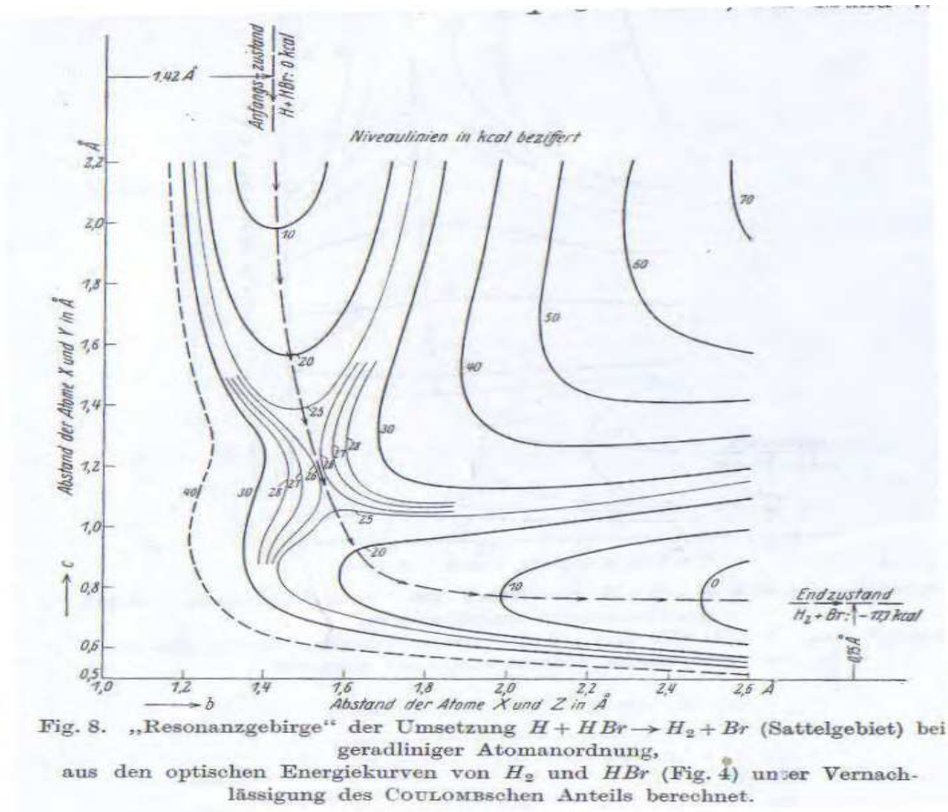


Fig. 8. „Resonanzgebirge" der Umsetzung $H + HBr \rightarrow H_2 + Br$ (Sattelgebiet) bei geradliniger Atomanordnung, aus den optischen Energiekurven von H_2 und HBr (Fig. 4) unter Vernachlässigung des COULOMBschen Anteils berechnet.

Fig. 10. Potential surface for the reaction H + HBr → H_2 + Br

6.2 TST presentation

The energetic description of all the configuration states of a chemical system was applied to Chemical Kinetics independently by the two researchers four years later, Polanyi from Manchester (Polanyi & Evans 1935) and Eyring from Princeton (Eyring 1935). The primacy is traditionally given to the most famous of the two, Eyring: the publications had some month of difference but the work was contemporary and a natural consequence of their previous joint work.

Absolute reaction rates are obtained statistically from the probability of rising of the reactants molecules from their fundamental state to the saddle of the maximum of the potential surface diagram (the activated complex). Evaluating the ratio of the partition functions of the activated and fundamental state of the reactants and the limitation of the degrees of freedom due to the particular geometry of the reaction surface (the saddle point of the activated complex reduce the degrees of freedom to one) Eyring obtained an Arrhenius type equation with a clear and definite value of the pre-exponential and exponent factors:

$$k = \left(\frac{k_b T}{h} \right) e^{-\frac{\Delta G^{\mp}}{RT}} \tag{16}$$

where $\Delta G^{\ddagger}$ is the Gibbs energy of activation, k_B is Boltzmann's constant, and h is Planck's constant. Eyring considered also the possible variations of the equation (16) due to the molecularity of the reaction.

The paper of Evans and Polanyi (Polanyi & Evans 1935) presented similar conclusions to that of Eyring but moreover tried to evaluate the interactions and energy exchanges between the reactants and the other actors of the chemical system (the solvent for example).

The investigations of Evans and Polanyi are not a simple detail, because they make evident the limits of the TST. The most known of them are the appearance of unexpected products due to particular form of the saddle surface, the tunnel effect through low energy barriers, the population of higher energy states rather than the only saddle state for high temperature reactions. A methodological limit is the vision of the process as a “big” isolated molecule where all the actors: reactants, activated complexes and products are contemporary presents and in equilibrium. This picture is valid when the main process is the establishment of the equilibrium between fundamental and activated states but results fallacious when other processes, as the interaction with solvent in diffusion controlled reactions for example become dominant. The other picture, less known, that sees the reaction as a process of diffusion will be examined in the next and last part of the chapter.

7. Genesis and development of diffusive-stochastic theories

The diffusion description, elaborated by Christiansen around 1935 (Christiansen 1936) and fully systematised in 1940 by Kramers (Kramers 1940), was an interesting and successful method complementary to transition state theory (TST). It received, however, little or no attention in chemistry circles for a long time (Zambelli 2010).

Hendrik Anthony Kramers (1894 –1952) was a Dutch physicist. He worked mainly in Germany and Denmark and was one of the most important collaborator of Bohr in the

famous Copenhagen Institute of Theoretical Physics. His interest in Chemical Kinetics derived from the collaboration with **Jens Anton Christiansen** (1888–1969), later full professor of Physical Chemistry at the Copenhagen University, around 1922.

Christiansen visited the Bohr Institute after his PhD graduation for a period of nearly one year. It is possible that he already came to Copenhagen with the hope of finding some mathematical-physical assistance for his studies of chemical reactions. Christiansen's studies treated the dynamics of specific chemical reactions: in this PhD Thesis he introduced for the first time the term *chain reactions* (*ketten reaction* in Danish). His developments in this field together with that of Bodenstein previously cited resulted fundamental for the work of **Nikolay Semenov** (1896-1986) and **Cyril Norman Hinshelwood** (1897-1967) that will produce a definitive theory on chain reactions around 1950.

7.1 Christiansen's approach

Christiansen tried to apply the description and the model of chain reactions to different mechanisms (Christiansen 1922) and wrote a paper with Kramers in 1923, cited previously, about unimolecular reactions confronting the activation mechanism due to thermal collisions and radiation absorption. They treated the radiation mechanism with the fundamental Einstein's quantum theory about matter-radiation interaction (Einstein 1917). Other work of Einstein and Smoluchowski will be necessary later for Christiansen-Kramers approach. After the paper the collaboration probably ended and the two researchers will reconsider separately these arguments around fifteen years later.

Christiansen developed the model of a chemical reaction as an intra-molecular diffusion process in the half of the thirties. He published two papers in 1935 (Christiansen 1935) and 1936 (Christiansen 1936) on this research. The paper of 1936 is particularly significant. Christiansen confronted Arrhenius's theory of activated states with a little known theory (Nernst 1893) of **Walther Hermann Nernst** (1864–1941). In Nernst's theory, the reaction velocity is obtained, by analogy with Ohm's law, as the ratio between a chemical potential and a chemical resistance. Christiansen intended the chemical potential as the difference of the chemical activities of the beginning and the final states and the chemical resistance was represented by a particular integral depending on temperature and diffusion constant. The purpose of Christiansen was to demonstrate, extending Arrhenius's conception, that the methods of Nernst and Arrhenius are analogous. The generalization of Arrhenius's theory is obtained by supposing an open, possibly infinite, sequence of many consecutive steps, thus gaining an expression consistent with that of Nernst. Christiansen discretized a chemical reaction considering not only one activated state, as in Arrhenius's model, but a series of consecutive n stages which result in reciprocal virtual equilibrium. The equilibria between reactants, products and intermediates are supposed to be valid because Christiansen considered the quantity of intermediates constant during the slow stages of reaction, so the process is stationary or quasi-stationary. These are a group of assumptions similar to those made in the theory of diffusion. In fact, according to Christiansen's hypothesis, the equilibrium quantity of the activated complexes may be put in relationship to the concentrations of a diffusing substance along the sections of a column. From this diffusive description, he obtained an expression for the reciprocal reaction rate which was consistent with that obtained on a thermodynamic basis. Christiansen expressed the velocity of reaction v in the form of a diffusion equation:

$$v = -\frac{D}{\varphi}\frac{\partial c\varphi}{\partial x} \tag{17}$$

Where D and φ are the diffusion and activity coefficients, c the concentration and x a reaction coordinate. This expression implies that the transport of molecules is produced by the concentration gradient and by molecular forces (their contribution represented by the activities φ). From (17) and other assumptions about the activity coefficient Christiansen obtained another equation analogous to that of Einstein and Smoluchowski about Brownian motion:

$$v = -D\frac{\partial c}{\partial x} + \frac{D}{RT}cK \tag{18}$$

The generalization of the Arrhenius conception brings us naturally to consider the transformation of a molecule during a reaction as an intra-molecular diffusion. To demonstrate this generalization Christiansen made some fundamental assumptions. He considered the case of a simple potential barrier, a symmetrical bi-stable one as shown in Fig. 11. This case will be examined better thanks to Kramers work of 1940.

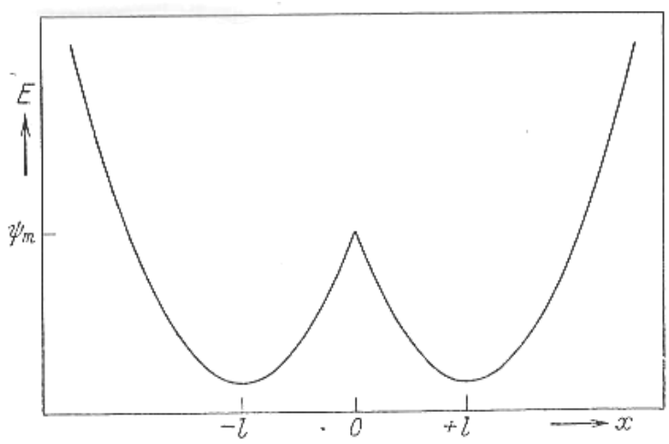


Fig. 11. Bi-stable potential barrier, the figure is taken from Christiansen's paper

7.2 The application of Klein-Kramers equation to chemical kinetics

The main biographers of Kramers, in particular Dirk ter Haar, claim that his interest in Chemical kinetics is a simple mathematical exercise of style. This may be partially true but Kramers's work would be impossible without Christiansen's previous contribution and his collaboration with **Oskar Benjamin Klein** (1894–1977) a Swedish theoretical physicist student of Arrhenius that during the years from 1917 to 1921 travelled many times back and forth between Copenhagen and Stockholm to complete his PhD thesis in which he examined the forces between ions in strong electrolyte solutions. The result was a generalized description of liquid dynamics and the formulation of what we call today the Klein–Kramers equation (Klein 1922).

Kramers paper of 1940 presents what today we call the "Kramers problem": the dynamics of a particle moving in a bi-stable external field of force, subject to the irregular forces of a

surrounding medium in thermal equilibrium. The particle, originally caught in a potential well, may escape by passing over a potential barrier. Constructing a diffusion equation for the density distribution of particles in phase space it is possible to calculate the probability and the escape rate as a function of the temperature and viscosity of the medium. Kramers considered the one dimensional motion of a particle of unit mass starting from a Langevin equation of the system for the time derivative of the velocity v:

$$\frac{dv}{dt} = -\xi v + f(t) - \frac{dV(x)}{dx} \tag{19}$$

where $V(x)$ is the potential field, ξ the friction and $f(t)$ a time dependent stochastic force. Searching for the distribution law of the particle in phase space on the basis of a given distribution of the random forces he obtained the diffusion equation for the particle distribution from the statistical moments of the random force:

$$\frac{\partial P(x, x_0, v, v_0, t)}{\partial t} = -\Gamma P(x, x_0, v, v_0, t) \tag{20}$$

Where the operator Γ is defined as:

$$\Gamma = v\frac{\partial}{\partial x} - \frac{dV(x)}{dx}\frac{\partial}{\partial v} - \xi\frac{\partial}{\partial v}\left(v + k_B T\frac{\partial}{\partial v}\right) \tag{21}$$

This express the Klein-Kramers equation of the system. Kramers found solutions of equation (21) in the stationary cases in a good range of viscosity. We remark that the stationarity condition is not strictly an approximation, but rather the simplest case of a non-equilibrium state of a system. If we consider the potential surface of a chemical system and assume the role of the solvent in the viscosity coefficient Kramers approach describes efficiently the course of chemical reactions.

8. Conclusions

Kramers found the Eyring-Polanyi equation (16) as a particular case of medium-small viscosity. It may seem impressive to see that the results of TST, based on quantum mechanics, come out as a particular case of Kramers pure classical method. But there are precise limitations to the use of Kramers method.

Methodologically, even if the diffusive stochastic approach has some theoretical advantages, it is more difficult to adapt and apply to the description of chemical reactions than TST. It requires notable mathematical knowledge and physical concepts that are not so familiar in chemistry. TST on the other hand, relying on the powerful means of quantum mechanics, produces more predictive results, although we have to apply phenomenological coefficients in some cases and make some arbitrary assumptions.

Diffusion approach, although less known, and TST represents the basic theories for contemporary studies on Chemical Kinetics, a disciple that now is a part of Physical Chemistry but that before Quantum Mechanics corresponded practically to it and that contributed so deeply, as we have seen, to the whole construction of Chemical Science.

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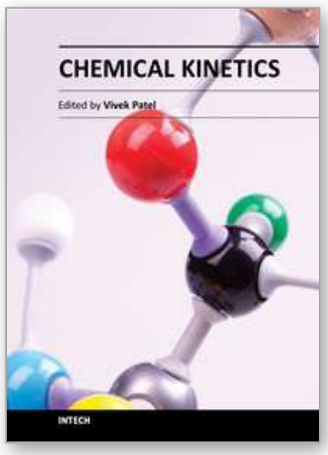

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Chemical Kinetics relates to the rates of chemical reactions and factors such as concentration and temperature, which affects the rates of chemical reactions. Such studies are important in providing essential evidence as to the mechanisms of chemical processes. The book is designed to help the reader, particularly students and researchers of physical science, understand the chemical kinetics mechanics and chemical reactions. The selection of topics addressed and the examples, tables and graphs used to illustrate them are governed, to a large extent, by the fact that this book is aimed primarily at physical science (mainly chemistry) technologists. Undoubtedly, this book contains "must read" materials for students, engineers, and researchers working in the chemistry and chemical kinetics area. This book provides valuable insight into the mechanisms and chemical reactions. It is written in concise, self-explanatory and informative manner by a world class scientists in the field.

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